4 Lattice Vibrations

Q. 4.1. (*a*) Explain briefly quantisation of lattice vibrations.

(*b*) Explain the concept of phonon. Which statistics does it obey?

(*c*) Give an evidence for the existence of phonons.

(*d*) Derive an expression for the energy and momentum of phonons and explain 'normal' process and Umklapp process.

(*e*) Discuss the inelastic scattering of photons by phonons and obtain an expression for the frequency of phonon emitted in the process. ***(G.N.D.U. 2000, 1997, 1996; Pbi.U. 2000, 1999, 1997; P.U. 2004, 2000, 1999, 1997, 1994; H.P.U. 2002, 1999, 1997, 1994)***

Ans. (*a*) Quantisation of lattice vibrations. A solid is composed of atoms or molecules which are closely packed. This is because atoms and molecules attract each other. As the distance between the atoms or molecules is made smaller and smaller a stage reaches when a repulsive force comes into play. At the equilibrium distance between the atoms or molecules the attractive and repulsive forces balance each other and the atom or molecule is fixed to this equilibrium position. The interatomic interaction, however, causes the atoms or molecules to vibrate about their mean position. As these atoms or molecules are present at the lattice points, these vibrations are known as *lattice vibrations*.

According to quantum theory, the energy of an elastic mode of vibration of angular frequency ω, when the mode is excited to a quantum number n is given by $E = \left(n + \frac{1}{2}\right)\hbar\omega$. The term $\frac{1}{2}\hbar\omega$ is the zero point energy of the mode. It occurs both for electromagnetic wave quanta-photons and elastic wave quanta-phonons as a consequence of their equivalence to a harmonic oscillator of angular frequency ω for which the energy eigenvalues are $\left(n + \frac{1}{2}\right)\hbar\omega$. The energy of a quantum of elastic wave of lattice vibration—the phonon—is, therefore quantised and each phonon is taken to have an energy $\hbar\omega$.

(*b*) **Phonon.** The energy in a lattice vibration or an elastic wave is quantised. Just as the quantum of energy in an electro-magnetic wave is a photon, the quantum of energy in an elastic wave is known as a *phonon*. A phonon wave travels in a medium with the velocity of sound v. The energy of a phonon is given by $h\nu = h\omega = h\nu K$, where h is Planck's constant ($\hbar = h/2\pi$), ν *the frequency,* ω *the angular frequency and* $\vec{K}$ *the wave vector* $\left(|\vec{K}| = \frac{2\pi}{\lambda}\right)$ *corresponding to the phonon wave.*

The vibration spectrum of the phonon wave occupies a wide range of frequencies from $10^4 - 10^{12}$ *Hz*. The low frequency part lies in the acoustic region and consists of sound waves in a crystal lattice. The high frequency part lies in the infra-red region and is due to thermal vibrations in a crystal analogous to thermally excited photons in black body radiation.

Statistics obeyed by phonons. Phonons like photons have zero spin. Hence phonons obey *Bose-Einstein statistics* and Bose-Einstein distribution law.

$$n = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Phonon representation. The pictorial representation of phonon is shown in Fig. 4.1 (*a*). The pictorial representation of photon is shown in Fig. 4.1 (*b*) for comparison.

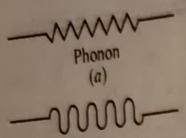

Fig. 4.1

(*c*) **Evidence for existence of phonons.** The experimental evidence that the energy of an elastic wave is quantised or for the existence of phonons "the quanta of lattice vibration energy" are:

(*i*) The lattice contribution to the heat capacity of solids approaches zero at absolute zero of temperature. This can be explained only if the lattice vibration is quantised.

(*ii*) Another experimental evidence for phonons is found in the inelastic scattering of *X*-ray photons (or neutrons) by crystals with momentum and energy changes according to the *creation* or *absorption* of one or more *phonons*.

(*d*) **Energy of phonon.** The energy of a phonon of frequency ν is given by $E = h\nu = \hbar\omega$

$= \hbar v \vec{K}$ where v is the velocity of phonon wave and $\vec{K}$ the phonon wave vector.

Momentum of a phonon. A phonon on a lattice really has no momentum in the physical sense. On the other hand, a phonon of wave vector $\vec{K}$ interacts with other particles such as photons, electrons and neutrons and fields as if it has a momentum $\hbar\vec{K}\left(\frac{h}{2\pi}\cdot\frac{2\pi}{\lambda} = \frac{h}{\lambda}\right)$, the same as for a photon of equivalent wavelength λ. The momentum $\hbar\vec{K}$ is called *crystal momentum*.

Normal process. In an elastic scattering of *X*-ray photon by a crystal, *i.e.*, Bragg's diffraction the wave vector conservation law gives

$$\vec{k'} = \vec{k} + \vec{G} \quad \ldots (i)$$

where $\vec{k}$ and $\vec{k'}$ are the wave vectors of incident and scattered photons respectively and $\vec{G}$ is the reciprocal lattice vector of the crystal. Equation (*i*) may be put in the form

$$\hbar\vec{k'} = \hbar\vec{k} + \hbar\vec{G}$$

In this process the crystal as a whole recoils with a momentum $\hbar\vec{G}$ and the frequency of the incident photon remains unchanged, *i.e.*, $|\vec{k'}| = |\vec{k}|$

Such a process in which the frequency of the incident photon is the same as that of the scattered photon is called normal or N-process. In this process no phonon is created or absorbed.

Umklapp process. In an inelastic scattering of a photon by a crystal, the frequency of the incident photon changes and a new photon is emitted alongwith a phonon which may be emitted or absorbed.

If a phonon of wave vector $\vec{K}$ is emitted or created during the scattering, then according to wave vector conservation law

$$\vec{k'}\ (\text{scattered}) + \vec{K} = \vec{k}\ (\text{incident}) + \vec{G}$$

or $$\hbar\vec{k'} + \hbar\vec{K} = \hbar\vec{k} + \hbar\vec{G}$$

If a phonon of wave vector $\vec{K}$ is absorbed during the scattering, then according to the wave vector conservation law

$$\vec{k'}\ (\text{scattered}) = \vec{k}\ (\text{incident}) + \vec{K} + \vec{G}$$

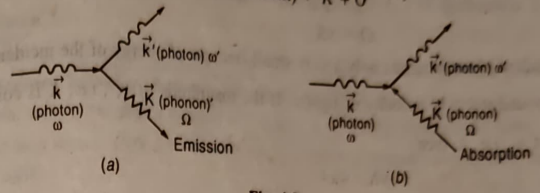

Fig. 4.2

The emission and absorption of phonon in inelastic scattering is shown in Fig. 4.2 (*a*) and (*b*) respectively.

Such a process in which the frequency of the photon changes is called umklapp (after the German for flipping over) or *U-process*. In this process, a phonon is created or absorbed in addition to the Bragg reflection and the momentum is transferred to the crystal as a whole.

(*e*) **Inelastic scattering of photons by phonons.** In an elastic scattering of *X*-ray photons by a crystal there is only a change in direction of the wave vector $\vec{k}$ of the incident photon but the magnitude of the wave vector (or the frequency) remains unchanged.

In inelastic scattering of photon by a crystal the frequency of the incident photon also changes and a *phonon* is emitted or absorbed. The frequency of the emitted phonon is such that:

Energy of incident photon = Energy of scattered photon + energy of emitted phonon

and Momentum of incident photon = momentum of scattered photon + momentum of emitted phonon.

Consider a photon of frequency $\nu = \omega/2\pi$ which is propagating in a crystal considered to be a continuum of refractive index μ. The velocity of photon in the medium is c/μ where c is the velocity of light in vacuum. The wave vector of the photon is given by

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{c/\mu}\cdot\frac{\omega}{2\pi} = \frac{\omega\mu}{c} \quad \ldots (i)$$

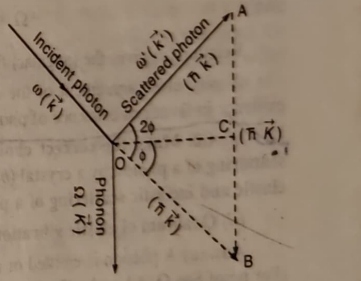

Fig. 4.3

Suppose the photon interacts with a phonon beam (sound wave) in the crystal and is scattered. This is because the refractive index of the crystal changes due to change in concentration of atoms brought about by the elastic strain field of the sound waves. In the inelastic scattering of the photon by the crystal a phonon is either created or absorbed. Let the wave vector of the photon change from $\vec{k}$ to $\vec{k'}$ and the frequency from ω to ω′ due to inelastic scattering and a phonon of wave vector $\vec{K}$ and frequency Ω be created as shown in Fig. 4.3.

Then, according to the **law of conservation of energy**

$$\hbar\omega = \hbar\omega' + \hbar\Omega \quad \ldots (ii)$$

and according to the **principle of conservation of momentum**

$$\hbar\vec{k} = \hbar\vec{k'} + \hbar\vec{K}$$

If the velocity of sound v is a constant, then (angular) frequency Ω of the phonon of wave vector of magnitude K is given by

$$v = \frac{\Omega}{2\pi} \cdot \frac{2\pi}{K} = \frac{\Omega}{K}$$

or $$\Omega = vK \quad \ldots (iii)$$

The emitted phonon carries only a very small fraction of energy of the incident photon. The velocity of sound $v \ll$ the velocity of light c. If the magnitude of $\vec{K}$, *i.e.*, K is comparable with magnitude of $\vec{k}$, *i.e.*, k, then

$$vK \ll ck$$

Also $\omega = ck$ and $\Omega = vK$

$$\therefore \quad \omega \gg \Omega \quad \ldots (iv)$$

Hence from (*ii*), we have $\omega' \simeq \omega$ and, therefore, $k' \simeq k$

The momentum of the photon as well as the phonon is proportional to and in the direction of corresponding wave vector. Therefore, OAB is the momentum vector diagram. According to relation (*iv*), the magnitude of k' is very nearly equal to that of k. Taking $k' = k$ we have $OA = OB$ and the $\Delta\, OAB$ is isosceles.

$$\therefore \quad AB = \text{magnitude of } \vec{K} = 2k \sin\phi$$

where $\angle AOB = 2\phi$ and OC is perpendicular to AB.

But from relation (*i*) $k = \dfrac{\omega\mu}{c}$

$$\therefore \quad K = \frac{2\omega\mu}{c} \sin\phi$$

and $$\Omega = vK = \frac{2v\,\omega\,\mu}{c} \sin\phi \quad \ldots (v)$$

Relation (*v*) gives the (angular) frequency of the emitted phonon.

A very close agreement of the calculated and experimental values of Ω is a very strong evidence in favour of existence of phonons and their behaviour.

Q. 4.2. Make the correct choice. (*i*) A phonon is emitted or absorbed in (*a*) elastic scattering of a photon by a crystal (*b*) inelastic scattering of a photon by a crystal (*c*) Both the elastic and inelastic scattering of a photon by a crystal (*d*) None of these. ***(H.P.U 1997)***

(*ii*) Quantum of elastic vibration is (*a*) photon (*b*) phonon (*c*) graviton. ***(H.P.U. 2001)***

Ans. (*a*) A phonon is emitted or absorbed in the inelastic scattering of a photon by a crystal (For proof **See Q. 4.1** under **'Umklapp process'**.

(*b*) Phonon.

Q. 4.3. (*a*) State the concepts which are common to both photons and phonons.

(*b*) What is the difference between photons and phonons?

(Pbi.U. 2004, 2003; G.N.D.U. 2003; P.U. 2003)

Ans. (*a*) **Concepts common to photons and phonons.** (*i*) A photon and a phonon both exhibit wave particle duality.

(*ii*) The energy of a photon of frequency ν is $h\nu$. The same is true of a phonon as its energy is also $h\nu = \hbar\omega$ where ω is the frequency of vibration.

(*iii*) The momentum of a photon $p = \dfrac{h}{\lambda} = hk$ where k is the propagation constant.

Although a phonon in a lattice really has no momentum in the physical sense, a phonon of wave vector $\vec{K}$ interacts with other particles such as photon, electron etc. as if it has a momentum $\hbar\vec{K} = \dfrac{h}{\lambda}$, the same as for a photon of equivalent wavelength λ. The momentum $\hbar\vec{K}$ is called *crystal momentum*.

(*iv*) Phonons are indistinguishable particles like photons and also obey Base Einstein statistics.

(*b*) **Difference between photons and phonons.** (*i*) A photon is a quantum of energy in electromagnetic waves, whereas a phonon is a quantum of energy in an elastic wave.

(*ii*) A photon travels with the velocity of light whereas phonon travels with the velocity of sound in the solid.

(*iii*) Photons do not require any material medium for their propagation, *i.e.*, photon can travel through vacuum whereas phonons do require a material medium to travel, *i.e.*, they cannot travel through vacuum.

(*iv*) A phonon is emitted or absorbed in the inelastic scattering of a photon by a crystal. The reverse process, *i.e.*, emission or absorption of a photon by scattering of a phonon is not possible.

Q. 4.4. Show that the dispersion relation for the lattice waves in a monatomic linear lattice of mass m, spacing a and nearest neighbour interaction C is $\omega = 2\sqrt{\dfrac{C}{M}} \sin\left|\dfrac{1}{2}\vec{k}a\right|$ where ω is the angular frequency and $\vec{k}$ the wave vector. What are the allowed values of phonon wave vector? ***(Meerut U. 2003; Pbi.U. 2002, 2001; G.N.D.U. 2000, 1997; A.U. 1994; H.P.U. 1994; P.U. 1991)***

Ans. Lattice waves in a monatomic linear lattice. To study the vibrations of one dimensional monatomic lattice, consider the vibrational motion of a non-homogeneous medium, *e.g.*, a linear chain of identical atoms of mass m spaced at a distance a – the lattice constant, connected by ideal springs. In practice this is met with, in the case of elastic vibrations of a crystal with one atom in the primitive cell. When a wave propagates in such a cubic crystal along the directions [100], [110], [111], the entire planes of atoms move in phase with displacements either parallel or perpendicular to the direction of the wave vector. In such a case the displacement of a plane from its equilibrium position can be described by a *single* coordinate, *i.e.*, the problem becomes *one dimensional*. However, for each wave vector there are *three* modes–one of longitudinal polarisation and two of transverse polarisations.

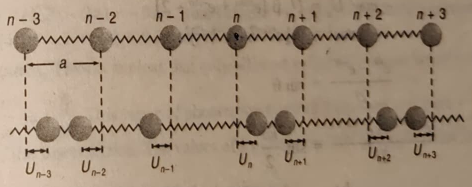

Fig. 4.4

Let the single coordinate be x. The co-ordinate of the nth atom is represented by $x = na$. Thus at equilibrium the atoms are situated at *equally spaced sites* represented by ..... $n-3$, $n-2$, $n-1$, n, $n+1$, $n+2$, $n+3$, ... with x coordinates as $(n-3)\,a$, $(n-2)\,a$, $(n-1)\,a$, na, $(n+1)\,a$, $(n+2)\,a$, $(n+3)\,a$, and so on.

As the atoms in the crystal start vibrating, let U_n denote the displacement of the nth atom, then U_{n-1}, U_{n+1}, U_{n-2}, U_{n+2}, ... denote the displacement of $n-1$, $n+1$, $n-2$, $n+2$th atom respectively.

Let β be the *spring constant* or *stiffness* or nearest neighbour interaction given by the relation

$$F = \beta U$$

where F is the applied force and U the displacement of the corresponding atom. This means that the force required to produce an *atomic displacement* is proportional to the *displacement* itself. In other words, the vibrational motion of each atom is *simple harmonic*. Therefore, the net force acting on the nth atom in terms of the extensions of the two springs which bind it to the $(n-1)$th and $(n+1)$th atom is given by

$$F_n = \beta (U_{n+1} - U_n) - \beta (U_n - U_{n-1})$$
$$= \beta (U_{n+1} + U_{n-1} - 2U_n)$$

neglecting the direct effect of other atoms like $(n+2)$, $(n-2)$ ... etc which are supposed to act via atoms $(n+1)$ and $(n-1)$.

If $\frac{d^2U_n}{dt^2}$ denotes the acceleration of the nth atom,

then
$$m \frac{d^2U_n}{dt^2} = \beta (U_{n+1} + U_{n-1} - 2U_n) \quad \ldots (i)$$

This is a differential equation in displacements and has a periodic travelling wave solution of the type

$$U_n = U_0 e^{i(\omega t + kx)}$$

where ω and k are constants, ω being the angular frequency and k the wave vector.

Here $x = na$ where a is the spacing between the two nearest atoms of the linear chain. Thus

$$U_n = U_0 e^{i[\omega t + kna]}$$
$$U_{n+1} = U_0 e^{i[\omega t + k(n+1)a]} = U_0 e^{i[\omega t + kna]} e^{ika} = U_n e^{+ika}$$
$$U_{n-1} = U_0 e^{i[\omega t + k(n-1)a]} = U_0 e^{i[\omega t + kna]} e^{-ika} = U_n e^{-ika}$$

$$\frac{dU_n}{dt} = i\omega U_0 e^{i(\omega t + kna)}$$

and
$$\frac{d^2U_n}{dt^2} = -\omega^2 U_0 e^{i(\omega t + kna)} = -\omega^2 U_n$$

Substituting in (i), we have

$$-m\omega^2 U_n = U_n \beta [e^{+ika} + e^{-ika} - 2]$$

or
$$-m\omega^2 = \beta [e^{+ika/2} - e^{-ika/2}]^2$$

Now,
$$\frac{e^{i\theta} - e^{-i\theta}}{2i} = \sin\theta$$

$\therefore$
$$\frac{e^{+ika/2} - e^{-ika/2}}{2i} = \sin\frac{ka}{2}$$

or
$$\sin^2\frac{ka}{2} = -\frac{1}{4}\left[e^{+ika/2} - e^{-ika/2}\right]^2$$

Hence
$$-m\omega^2 = -4\beta \sin^2\frac{ka}{2}$$

or
$$\omega^2 = 4\frac{\beta}{m}\sin^2\frac{ka}{2} \quad \text{or} \quad \omega = \pm 2\sqrt{\frac{\beta}{m}}\sin\frac{1}{2}(ka) \quad \ldots (i)(a)$$

Dispersion relation. If we denote the nearest neighbour interaction by C instead of β, we get

$$\omega = \pm 2\sqrt{\frac{C}{m}}\sin\frac{1}{2}ka \quad \ldots (ii)$$

The above relation is known as *dispersion relation* because ω depends upon the value of $\sin\frac{1}{2}ka$ which varies from + 1 to zero taking only *positive* values.

$\therefore$ Relation (ii) can be put as

$$\omega = \sqrt{\frac{4C}{m}}\left|\sin\frac{1}{2}ka\right| \quad \ldots (iii)$$

Allowed values of phonon wave vector. The energy in a lattice vibration or an elastic wave is quantised. By analogy with *photon* – the quantum of energy in an electromagnetic wave, the quantum of energy in an elastic wave is known as a *phonon*. A phonon wave travels in a medium with the velocity of sound v. The energy of a phonon is given by $h\nu = h\omega = \hbar nk$ where h is Planck's constant ($h = h/2\pi$), ν the frequency, ω the angular frequency, and $\vec{k}$ the wave vector $\left(k = |\vec{k}| = \frac{2\pi}{\lambda}\right)$ corresponding to the phonon wave.

A graph between ω taken along the Y-axis and values of k taken along the X-axis from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$ is shown in Fig. 4.5.

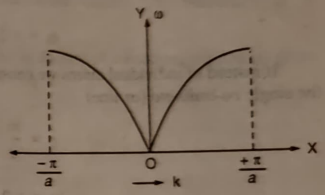

Fig. 4.5

For elastic waves only those values of *phonon wave vector* are *allowed* (significant) for which the *phase ka* lies between $-\pi$ and $+\pi$ or k lies between $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$. We take both positive and negative values of k because the wave can propagate to the right ($+x$ direction) as well as to the left ($-x$ direction).

For any other value of relative phase ka say $ka = 1.2\pi$ $\left(\text{or } k = 1.2\frac{\pi}{2}\right)$, it is equivalent to a relative phase $ka = (1.2\pi - 2\pi) = -0.8\pi$ lying between $-\pi$ and $+\pi$. Similarly a relative phase of 4.2π is equivalent to $(4.2\pi - 2 \times 2\pi) = 0.2\pi$ which again lies between $-\pi$ to $+\pi$.

Brillouin zones. Thus it is clear that only allowed values of phonon wave vector k are those lying between $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$. This range of phonon wave vector k between $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ gives the *first* Brillouin zone of the linear lattice. The values of k outside the first Brillouin zone simply reproduce lattice motions described by values with the limits $\pm\frac{\pi}{a}$.

In general, let the value of k lying between $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ corresponding to a vibrational motion of the lattice of frequency ω_0 be k_0. If k is another value given by

$$k = k_0 - \frac{2\pi}{a}n, \quad \text{where } n \text{ is an integer, then}$$

$$\sin\frac{ka}{2} = \sin\left(k_0 - \frac{2\pi}{a}n\right)\frac{a}{2} = \sin\left(k_0\frac{a}{2} - n\pi\right)$$

$$= \left|\sin k_0\frac{a}{2}\right|$$

Thus, the vibrational motion of the lattice corresponding to k is also ω_0. In other words, associated with a given frequency ω_0 there are many possible values of wave vector k, *i.e.*, the lattice can propagate several wavelengths at the same frequency ω_0.

Q. 4.5. (*b*) State the dispersion relation for the lattice waves in a monatomic linear lattice in terms of wave velocity. Discuss the dispersion behaviours (*i*) at low frequencies (*ii*) at high frequencies and (*iii*) at maximum frequency of vibration.

(*b*) Compute the cut off frequency for a linear monoatomic lattice if the velocity of sound and inter atomic spacing in the lattice are 3×10^3 ms^{-1} and 3×10^{-10} m respectively.

(*Pbi.U. 2000*)

Ans. (*a*) **Dispersion relation in terms of wave velocity.** The dispersion relation for the lattice waves in a monatomic linear lattice of mass m spacing a and β the stiffness or the nearest neighbour interaction is given by (according to relation [(*i*) (*a*) **Q. 4.4**]

$$\omega = \pm 2\sqrt{\frac{\beta}{m}}\sin\frac{1}{2}ka \qquad \ldots (i)$$

If instead of individual atoms we consider the entire crystal plane, then the *linear density* along the single *co-ordinate* (or line)

$$\rho = \frac{m}{a} \quad \text{or} \quad m = a\rho$$

$$\omega = \pm 2\sqrt{\frac{\beta}{a\rho}}\sin\frac{1}{2}ka$$

If E is the longitudinal stiffness (or elasticity), then $E = \beta a$ or $\beta = \frac{E}{a}$

$$\therefore \quad \omega = \frac{2}{a}\sqrt{\frac{E}{\rho}}\sin\frac{1}{2}ka$$

But $\sqrt{\frac{E}{\rho}} = v_0$ the velocity of the wave along the line

$$\therefore \quad \omega = \frac{2}{a}v_0\left|\sin\frac{ka}{2}\right| \text{ taking only positive values.}$$

(*i*) **At low frequencies.** For values of $k \to 0$, $\sin\frac{ka}{2} = \frac{ka}{2}$ because for small values of θ, $\sin\theta = \theta$

$$\therefore \quad \omega = \frac{2}{a}v_0\frac{ka}{2} = v_0 k$$

In this case phase velocity $v_p = \frac{\omega}{k} = v_0$ ... (*ii*)

and group velocity $v_g = \frac{d\omega}{dk} = v_0$ ... (*iii*)

i.e., phase velocity = group velocity = v_0

The relation $v_0 = \frac{\omega}{k}$ is the same as that for a homogeneous continuous line. Thus for long wavelength the atomic nature of linear chain has no importance, so for as the dynamical behaviour of the system is concerned, *i.e.*, the discrete nature of the structure is not sensitive to long wavelengths. In other words, a large number of atoms together participate in all displacements as on a homogeneous line.

(*ii*) **At high frequencies.** At high frequencies

Phase velocity $v_p = \frac{\omega}{k} = \frac{2}{ka}v_0\sin\frac{ka}{2}$ ... (*iv*)

and group velocity $v_g = \frac{d\omega}{dk} = v_0\cos\frac{ka}{2}$ ... (*v*)

Thus both the velocities are a function of frequency. This is similar to the optical case in which as light passes through a medium the refractive index being a function of frequency is responsible for the phenomenon of dispersion of light. By analogy the present medium is also said to be *dispersive*.

(*iii*) ***At frequency*** $\omega = \sqrt{4\frac{C}{m}}\left(\text{or }\sqrt{\frac{4\beta}{m}}\right)$ (*maximum value*). At frequency $\omega = \sqrt{4\frac{C}{m}}\left(\text{or }\sqrt{\frac{4\beta}{m}}\right)$ which represents the maximum angular frequency of vibration, relation (*i*) gives

$$\sin\frac{1}{2}ka = 1 \quad \text{or} \quad \frac{ka}{2} = \frac{\pi}{2}$$

$$\therefore \quad k = \frac{\pi}{a} \quad \text{or} \quad \frac{2\pi}{\lambda} = \frac{\pi}{a}$$

$$\lambda = 2a$$

Substituting, $k = \frac{\pi}{a}$ and $\frac{ka}{2} = \frac{\pi}{2}$ in Eq. (*iv*), we get

$$v_p = \frac{2}{\frac{\pi}{a}a}v_0\sin\frac{\pi}{2} = \frac{2}{\pi}v_0 \qquad \ldots (vi)$$

Substituting $k = \frac{\pi}{a}$ and $\frac{ka}{2} = \frac{\pi}{2}$ in Eq. (*v*), we get

$$v_g = v_0\cot\frac{\pi}{2} = 0 \qquad \ldots (vii)$$

From Eqs. (*vi*) and (*vii*) we find that the group velocity is zero and phase velocity has a finite value $\frac{2v_0}{\pi}$. The group velocity represents the velocity of energy transmission or signal. Therefore, for values of $k = \frac{\pi}{a}$ there is no propagation of signal or energy, *i.e.*, the corresponding wave is a *standing wave*.

This situation is similar to Bragg condition of reflection of *X*-rays from successive pl
atoms in a crystal given by

$$2d \sin \theta = n\lambda$$

In the first order reflection ($n = 1$) and for normal incidence ($\theta = \frac{\pi}{2}$ or $\sin \theta = 1$), $\lambda =$

Compare with $\lambda = 2a$ given above. Thus at the edges of the Brillouin Zone $k = -\pi/a$ and $k =$

$v_g = 0$ – a condition necessary for standing waves.

Further such a linear chain can propagate waves (or vibrations) only of angular frequen

$$\omega \leq \frac{2}{a} v_0$$

Thus a monoatomic linear lattice acts as a low pass filter which allows only the frequenc
the range zero to $\frac{2v_0}{a}$. In other words, $\omega = \frac{2}{a} v_0$ is the maximum or *cut off* frequency for a
monoatomic lattice.

(*b*) Velocity of sound $v_0 = 3 \times 10^3$ ms^{-1}; Interatomic spacing in the lattice $a = 3 \times 10^{-10}$

$$\therefore \quad \text{Cut off frequency } \omega = \frac{2}{a} v_0 = \frac{2 \times 3 \times 10^3}{3 \times 10^{-10}} = 2 \times 10^{13} \text{ Hz}$$

**Q. 4.6. What is a phonon? Derive the vibrational modes of a diatomic linear la
Name the different branches of the dispersion relation curve. What is the difference bet
the two branches?** (*Meerut U.* **2002;** *Luck.U.* **2001, 1996, 1995;** *P.U.* **19**

Ans. Phonon. See Q. 4.1 (*b*) (phonon)

Vibrations of a one dimensional linear diatomic lattice. Consider a diatomic crystal suc
NaCl or diamond in which there are two atoms per unit primitive cell. Let the distance betw
nearest neighbours be '*a*' so that the *repeat distance*' is 2*a*. Let the mass of one atom be *m* and
of the other *M* ($m < M$). These atoms are placed alternately along the *X*-axis and in a stat
equilibrium let these atoms be at places..... $(2n-3)$, $(2n-2)$, $(2n-1)$, $2n$, $(2n+1)$, $(2n$
$(2n+3)$ ..... the atoms of mass *m* are at even numbered points and those of mass *M* at
numbered points. Let U_{2n} be the displacement of the atom corresponding to the $2n$th site at any
during the vibratory motion of the atoms.

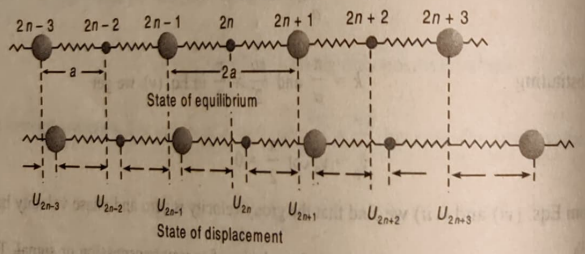

Fig. 4.6

By analogy with the monoatomic case and using similar assumptions we obtain the follow
two equations of motion, one for the lighter atom (mass *m*) and the other for the heavier atom (m
M).

For atoms of mass *m* at *even* points

$$F_{2n} = m \frac{d^2U_{2n}}{dt^2} = \beta (U_{2n+1} + U_{2n-1} - 2U_{2n}) \quad \ldots (i)$$

For atoms of mass *M* at *odd* points

$$F_{2n+1} = M \frac{d^2U_{2n+1}}{dt^2} = \beta (U_{2n+2} + U_{2n} - 2U_{2n+1}) \quad \ldots (ii)$$

The solution of these equations in the form of travelling waves with different amplitudes is given by

$$U_{2n} = A \exp i [\omega t - 2n\, ka]$$

Similarly,
$$U_{2n+1} = B \exp i [\omega t - (2n+1)\, ka]$$
$$U_{2n+2} = A \exp i [\omega t - (2n+2)\, ka]$$

and
$$U_{2n-1} = B \exp i [\omega t - (2n-1)\, ka]$$

where *k* is the wave vector of a particular mode of vibration. The vibrational frequency of both the types of atoms have been taken to be the same because both types of atoms participate in the same wave motion. The amplitudes *A* and *B* are different because of different masses of the atoms

Now,
$$\frac{d^2U_{2n}}{dt^2} = -A\omega^2 \exp i [\omega t - (2n)\, ka]$$

Hence,
$$m \frac{d^2U_{2n}}{dt^2} = -Am\omega^2 \exp i [\omega t - (2n)\, ka]$$

$$\therefore -Am\omega^2 \exp i [\omega t - (2n)\, ka] = \beta B \{\exp i [\omega t - (2n+1)\, ka] + \exp i [\omega t (2n-1)\, ka]\} - 2\beta A \exp i [\omega t - (2n)\, ka]$$

or
$$-m\omega^2 A = \beta B (e^{ika} + e^{-ika}) - 2\beta A \quad \ldots (iii)$$

Similarly,
$$\frac{Md^2U_{2n+1}}{dt^2} = -BM\omega^2 \exp i [\omega t - (2n+1)\, ka]$$

$$\therefore -M\omega^2 B \exp i [\omega t - (2n+1)\, ka] = \beta A \{\exp i [\omega t - (2n+2)\, ka] + \exp i [\omega t - (2n)\, ka]\} - 2\beta B \exp i [\omega t - (2n+1)\, ka]$$

or
$$-M\omega^2 B = \beta A (e^{ika} + e^{-ika}) + 2\beta B \quad \ldots (iv)$$

Now,
$$e^{ika} + e^{-ika} = 2 \cos ka$$

$\therefore$ Eq. (*iii*) becomes $(2\beta - m\omega^2) A - (2\beta \cos ka) B = 0 \quad \ldots (v)$

and Eq. (*iv*) becomes $(-2\beta \cos ka) A + (2\beta - \omega^2 M) B = 0 \quad \ldots (vi)$

This system of homogeneous linear equations has a non-zero solution for *A* and *B* only if the determinant of the coefficient of *A* and *B* is zero, *i.e.*,

$$\begin{vmatrix} 2\beta - m\omega^2 & -2\beta \cos ka \\ -2\beta \cos ka & 2\beta - M\omega^2 \end{vmatrix} = 0$$

or
$$(2\beta - M\omega^2)(2\beta - m\omega^2) - 4\beta^2 \cos^2 ka = 0$$

or
$$4\beta^2 - 2\beta m\omega^2 - 2\beta M\omega^2 + Mm\omega^4 - 4\beta^2 \cos^2 ka = 0$$

or
$$\omega^4 - 2\beta \frac{(m+M)}{mM} \omega^2 + \frac{4\beta^2}{mM} (1 - \cos^2 ka) = 0$$

or
$$\omega^4 - 2\beta \frac{(m+M)}{mM} \omega^2 + \frac{4\beta^2}{mM} \sin^2 ka = 0$$

This is a quadratic equation in ω^2 and gives the value of ω^2 as

$$\omega^2 = \beta\left[\frac{1}{m}+\frac{1}{M}\right] \pm \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 ka}{mM}} \quad \ldots (vii)$$

This is the dispersion relation for a linear diatomic lattice. The corresponding dispersion relation for a monatomic lattice is

$$\omega^2 = \frac{4\beta}{m}\sin^2\frac{ka}{2}$$

Since ω should be positive each value of ω^2 leads to a single value of ω. Thus we find that in the monatomic case there is only one value of ω for a single value of k whereas in the diatomic case there are two values of ω. These values are denoted as ω_+ and ω_-

$$\therefore \quad \omega_+^2 = \beta\left[\frac{1}{m}+\frac{1}{M}\right] + \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 ka}{mM}} \quad \ldots (viii)$$

and

$$\omega_-^2 = \beta\left[\frac{1}{m}+\frac{1}{M}\right] - \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 ka}{mM}} \quad \ldots (ix)$$

Different branches of the dispersion relation curve. The graph between ω and k leads to two branches: one corresponding to ω_+ and is called *optical branch* and the second corresponding to ω_- and is called the *acoustical branch* as shown in Fig. 4.7.

(*i*) **Optical branch (case of ω_+).** In the case of ω_+ for $k \to 0$, $\sin ka \to 0$, *i.e.*, it is negligible. Therefore, putting $\sin ka = 0$ in Eq. (*viii*), we get

$$\omega_+ = \sqrt{2\beta\left(\frac{1}{m}+\frac{1}{M}\right)} \quad \ldots (x)$$

For $k \to \frac{\pi}{2a}$, $\sin ka \to 1$, and we have

$$\omega_+^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) + \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4}{mM}}$$

$$= \beta\left(\frac{1}{m}+\frac{1}{M}\right) + \beta\left(\frac{1}{m}-\frac{1}{M}\right)$$

or

$$\omega_+ = \sqrt{\frac{2\beta}{m}} \quad \ldots (xi)$$

(*ii*) **Acoustical branch (case of ω_-).** In the case of ω_- for $k \to 0$, we write $\sin ka = ka$. We do not put $\sin ka = 0$ because if we do so the value of ω_- will be zero, which is not acceptable.

$$\therefore \quad \omega_-^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) - \beta\left(\frac{1}{m}+\frac{1}{M}\right)\sqrt{1 - \frac{4k^2a^2}{mM}\left(\frac{mM}{m+M}\right)^2}$$

$$= \beta\left(\frac{1}{m}+\frac{1}{M}\right)\left[1 - \sqrt{1 - \frac{mM}{(m+M)^2}4k^2a^2}\right]$$

$$= \beta\left(\frac{1}{m}+\frac{1}{M}\right)\left[1 - 1 + \frac{mM}{(m+M)^2}2k^2a^2 + \ldots\ldots\right]$$

[Using Binomial theorem and neglecting higher powers]

$$= \frac{2\beta}{m+M}k^2a^2$$

$$\therefore \quad \omega_- = ka\sqrt{\frac{2\beta}{(m+M)}} \quad \ldots (xii)$$

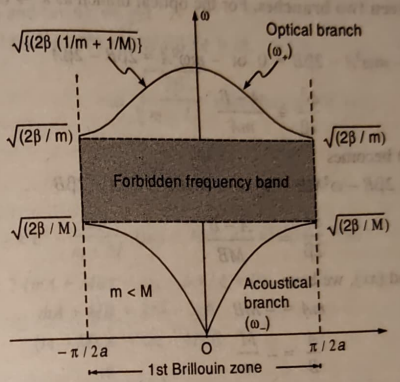

Fig. 4.7

For $k = \frac{\pi}{2a}$, we get a solution similar to result obtained in Eq. (*xi*) proved as under.

For $k = +\frac{\pi}{2a}$, the sine term becomes $\frac{-4}{mM}$, and we get

$$\omega_-^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) - \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4}{mM}}$$

$$= \beta\left(\frac{1}{m}+\frac{1}{M}\right) - \beta\left(\frac{1}{m}-\frac{1}{M}\right)$$

or

$$\omega_- = \sqrt{\frac{2\beta}{M}} \quad \ldots (xiii)$$

The complete curves for ω_+ and ω_- versus k are shown in Fig. 4.7.

Forbidden band. It is clear from Fig. 4.7, that wave like solutions do not exist for frequency lying between $\sqrt{\frac{2\beta}{m}}$ and $\sqrt{\frac{2\beta}{M}}$. In other words, there is a band of frequencies between the two branches which cannot propagate. This band is known as *Forbidden Frequency band*. The width of the forbidden band depends upon the difference of masses. The larger the mass ratio $\frac{M}{m}$ the wider the frequency gap between the two branches. If $M = m$, the optical and the acoustical frequency coincide at $k = \pm\frac{\pi}{2a}$ and the forbidden band vanishes. The first Brillouin zone is defined by k-values which lie in the range

$$-\frac{\pi}{2a} < k < \frac{\pi}{2a}$$

Thus, the smallest possible wavelength of this zone is $4a$ which corresponds to $k = \frac{\pi}{2a}$ at the zone boundary.

Difference between two branches. For the optical branch as $k \to 0$, $\cos ka \to 1$ and Eq. (v) becomes.

$$2\beta A - m\omega^2 A - 2\beta B = 0 \text{ or } -m\omega^2 A = 2\beta B - 2\beta A$$

or
$$\frac{\omega^2}{2\beta} = \frac{A-B}{mA} \quad \ldots (xiv)$$

Similarly Eq. (vi) becomes

$$-2\beta A + 2\beta B - \omega^2 MB = 0 \text{ or } -M\omega^2 B = 2\beta A - 2\beta B$$

or
$$\frac{\omega^2}{2\beta} = -\frac{A-B}{MB} \quad \ldots (xv)$$

From Eq. (xiv) and (xv), we have

$$mA = -MB$$

or
$$\frac{A}{B} = -\frac{M}{m} \quad \ldots (xvi)$$

This means that the two atoms move in opposite directions and their amplitudes are inversely proportional to their masses so that the centre of mass of the unit cell remains unchanged. Such a mode of vibration is shown in Fig. 4.8 (a).

For $M = m$, $\frac{A}{B} = -1$

Thus, even when their masses are equal, the atoms always move in opposite directions.

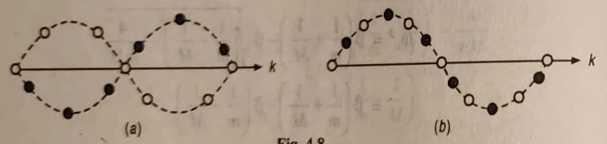

Fig. 4.8

For the acoustical branch as $k \to 0$

$$\cos ka = 1 - \frac{k^2a^2}{2} + \ldots\ldots \qquad \left[\because \cos\theta = 1 - \frac{\theta^2}{2} + \ldots\ldots\right]$$

In this case, the second term becomes significant and hence cannot be neglected. Eq. (v) now becomes

$$(2\beta - m\omega^2)A - 2\beta B\left[1 - \frac{k^2a^2}{2}\right] = 0$$

or
$$-m\omega^2 A = 2\beta B\left[1 - \frac{k^2a^2}{2}\right] - 2\beta A \quad \ldots (xvii)$$

Similarly, Eq. (vi) now becomes

$$-2\beta A\left[1 - \frac{k^2a^2}{2}\right] + (2\beta - \omega^2 M)B = 0$$

or
$$-M\omega^2 B = 2\beta A\left[1 - \frac{k^2a^2}{2}\right] - 2\beta B \quad \ldots (xviii)$$

Adding Eqs. $(xvii)$ and $(xviii)$, we get

$$-\omega^2(mA + MB) = -k^2a^2\beta(A + B)$$

But $\omega = ka\sqrt{\frac{2\beta}{m+M}}$ according to Eq. (xii)

$$\therefore \quad \omega^2 = k^2a^2\frac{2\beta}{m+M}$$

$$\therefore \quad -k^2a^2 \cdot \frac{2\beta}{m+M}(mA + MB) = -k^2a^2\beta(A + B)$$

or
$$2(mA + MB) = (m + M)(A + B)$$

or
$$mA + MB = MA + mB$$

or
$$(m - M)A = (m - M)B$$

$$\therefore \quad \frac{A}{B} = +1$$

This means that in the acoustical branch the two atoms of different masses move in the same direction with the same amplitude as shown in Fig. 4.8 (b).

In this case, there is a movement of their centres of masses as well. We, therefore, conclude that, in the optical case, the neighbouring atoms move in opposite directions whereas, in the acoustical case they move in the same direction.

The vibrations of the acoustical branch can be excited by a force which makes the atoms in a crystal move in the same direction such as sound waves. This is the reason why it is called acoustical branch. Monatomic crystals respond to such vibration.

The vibration of the optical branch can be excited by a force which makes the two neighbouring atoms move in opposite directions. The motion of this type can be excited by means of the electric field of the light waves which tends to move the ions in opposite directions.

The diamond and *hcp* lattices having two atoms per primitive cell exhibit optical branches.

To sum up:

(*i*) In diatomic lattice, the allowed frequencies constitute two frequency bands, one corresponding to the acoustical mode and the other to the optical mode of vibration.

(*ii*) If the masses m and M are equal, the frequency range in both the monatomic and diatomic lattice is the same. In this case, there is no forbidden band.

(*iii*) At the Brillouin zone edge $\left(k = \frac{\pi}{2a}\right)$ only one of the sub-lattice vibrates. The lighter atom (m) vibrates in the optical branch and the heavier atom (M) vibrates in the acoustical branch.

(*iv*) As the heavier mass M increases the optical branch flattens and the acoustical branch yields downward. For $M \to \infty$, the acoustical branch disappears and the optical branch becomes flat (parallel to k-axis).

(v) As the lighter mass m decreases, the optical branch moves upward while the acoustical branch is not effected. As $m \to 0$ the optical branch disappears altogether.

(vi) The optical mode is, in fact, the natural frequency of the lighter atoms (m) perturbed by the heavier sub-lattice. At $k = \frac{\pi}{2a}$ the heavy atom is stationary and the natural frequency of the vibrating lighter atom is $\sqrt{\frac{2\beta}{m}}$.

Q. 4.7. (*a*) Define 'Molar specific heat' (*i*) at constant pressure (*ii*) at constant volume and lattice heat capacity.

(*b*) Explain Dulong and Petit's law for the specific heat of a solid. Discuss the agreement of the result with that of the experiment. What discrepency was removed by Einstein?

(G.N.D.U. 2002; Gharwal U. 2000; Pbi U. 1999; Bang.U. 1996, 1995)

Ans. (*a*) Specific heat. In general, whenever heat is imparted to a body a part of it is used to increase its internal energy, *i.e.*, to raise its temperature and the rest in doing external work. If dQ is the heat energy absorbed by a system, dU the increase in internal energy, and dW the external work done by it, then if all quantities are measured in units of work, we have

$$dQ = dU + dW$$

If pressure remains constant at P and a change of volume dV takes place, then $dW = PdV$ and

$$dQ = dU + PdV \qquad \ldots (i)$$

If dT is the corresponding increase in temperature, then dQ/dT is known as specific heat of the substance.

There are in general two specific heats:

(*i*) Specific heat at constant pressure, and

(*ii*) Specific heat at constant volume.

Molar specific heat. If dQ is the amount of heat energy required to raise the temperature of one kilo-mole of a substance through dT °C keeping the pressure constant, then

Molar specific heat at constant pressure

$$C_p = \left(\frac{dQ}{dT}\right)_p$$

Similarly if dQ is the amount of heat energy required to raise the temperature of one kilo-mole of a substance through dT °C, keeping the volume constant, then

Molar specific heat at constant volume

$$C_v = \left(\frac{dQ}{dT}\right)_v$$

In case of solids the two specific heats do not differ much particularly at low temperatures as the volume expansion in solids is small. By the term specific heat of a solid we shall mean specific heat at constant volume.

Now, at constant volume $dV = 0$

$\therefore$ Relation (*i*) becomes

$$dQ = dU$$

Hence, $$C_v = \left(\frac{dQ}{dT}\right)_v = \left(\frac{dU}{dT}\right)_v$$

Lattice heat capacity. In solids the increase in internal energy takes place in two ways:

(*i*) Due to vigorous vibrations of atoms of the solid (assumed to be free) about their equilibrium positions as in crystals.

(*ii*) Due to thermal excitation of electrons to higher energy states as in metals and semiconductors.

If we denote the energy contribution due to atomic vibrations in crystal lattice as $U_{Lattice}$ and thermal excitation of electrons as U_{Elect} then

$$U = U_{Lattice} + U_{Elect}$$

and correspondingly, we have

$$C_v = \left(\frac{dU}{dT}\right)_v = \frac{d}{dt}(U_{Lattice}) + \frac{d}{dt}(U_{Elect})$$

$$= C_{Lattice} + C_{Elect}$$

The quantity $C_{Lattice}$ is known as lattice specific heat or *Lattice heat capacity*. In discussing the specific heat of solids like crystals, we assume that no free electrons are present and the entire specific heat of a crystal is due to the excitations of thermal vibrations of the lattice. Therefore, for our discussion

$$C_v = C_{Lattice}$$

(*b*) Dulong and Petit's law. According to classical theory, an atom is taken to be a point particle having no structure. It, therefore, has *three degrees of freedom*. According to kinetic theory, the average energy of a classical system is $\frac{1}{2}kT$ per degree of freedom where k is Boltzmann's constant. This result can be extended to particles interacting with harmonic forces. In such a case the *average kinetic energy* remains the same, *i.e.*, $\frac{1}{2}kT$ per degree of freedom and the *average potential energy* also has the same value, *i.e.*, $\frac{1}{2}kT$. Hence for particles which interact with harmonic forces the average *total energy* per degree of freedom $= \frac{1}{2}kT + \frac{1}{2}kT = kT$. As a point particle has three degrees of freedom the total energy per atom is $3\,kT$.

Therefore, the total vibrational energy of a crystal composed of N identical atoms can be written as

$$U = 3N\,kT$$

as a crystal is being taken equivalent to $3N$ harmonic oscillators.

It is supposed that atoms in a solid behave as free classical harmonic oscillators vibrating about their mean position which gives the lattice contribution to the molar heat capacity at constant volume.

As $$U = 3N\,kT$$

$$C_v = \left(\frac{dU}{dT}\right)_v = 3Nk = 3R$$

If N is equal to Avogadro's number, R is the universal gas constant having a value $R = Nk = 8.31 \times 10^3$ Joules/kilo-mole $K = 1.99$ kilo cal/kilo-mole K

$\therefore$ $$C_v = 3R = 5.97 \text{ kilo-cals/kilo-mole}$$

This result $C_v = 5.97$ = a constant is known as Dulong and Petit's law.

Agreement of results with experiments. According to Dulong and Petit's law and classical theory, specific heat is independent of temperature. This result is in quite good agreement with observed heat capacity of many solids including metals at high temperature but the classical formula breaks down at low temperatures. The specific heat of all solids drops sharply at low temperatures and approaches zero at temperatures approaching 0 K. This is against the Dulong and Petit's law.

A graph showing the variation of heat capacity with temperature for a typical case is shown in Fig. 4.9.

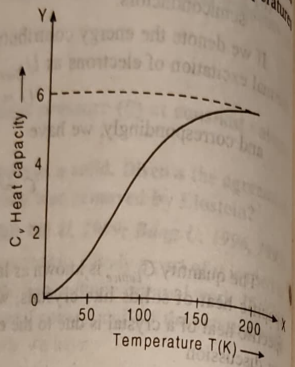

Fig. 4.9

(*i*) At high temperature $C_v = 3R$ per mole. This is in accordance with Dulong and Petit's law. This is true for several compounds and heavy elements.

(*ii*) For light elements (such as gases) the contribution at room temperature is less than $3R$.

(*iii*) At low temperature C_v decreases exponentially as the temperature is reduced and tends to zero as $T \to 0$.

In the temperature range 0 – 20 K

For non-metals $C_v = \alpha T^2$

For metals $C_v = \alpha T^3 + \gamma T$

(γ is volume expansion coefficient)

For layered compounds $C_v = \alpha T^2$

For linear chained compounds $C_v = \alpha T$

Discrepency removed by Einstein. In the derivation of Dulong and Petit's law on the basis of *classical theory*, it is assumed that each atom is a classical three dimensional harmonic oscillator which vibrates independently of all other atoms in the crystal and has any value of energy ranging *continuously* from zero to infinity.

The results obtained were not, however, in agreement with experimentally observed values and gave rise to a number of discrepencies stated above.

The discrepency in classical theory was removed by Einstein by the application of *quantum* theory. According to quantum theory, the energy spectrum of atomic oscillators is not continuous but has discrete values of energy given by $E_n = \left(n + \frac{1}{2}\right) h\nu$ where ν is the frequency of the oscillator, h the Planck's constant and $n = 0, 1, 2, \ldots$ etc. (integral values) called quantum number. According to this theory, the ground state energy of a harmonic oscillator is not zero (as assumed in classical theory) but has a value $\frac{1}{2} h\nu$. Thus, the atom has vibrational energy even at $T = 0$ K.

Q. 4.8. What are the assumptions of Einstein's theory of specific heat of solids? Derive relation for lattice heat capacity following Einstein model. Discuss the relation at very high and very low temperatures. Give the predictions of the model and compare with experimental observations. ***(G.N.D.U. 2004, 2003, 2002, 2001, 2000, 1999, 1997, 1995; Meerut U. 2003; H.P.U. 2002, 1999, 1995; K.U. 2001, 1996; Gharwal U. 2000; Gauhati U. 2000; P.U. 1997, 1995; Bang.U. 1995, 1994)***

Ans. Einstein theory of Lattice heat capacity (*specific heat*). The results of the classical theory of specific heat were not in agreement with experimental results for many solids particularly at low temperatures. The discrepancies in the classical theory of specific heat were removed by Einstein to some extent by the application of quantum theory. For this purpose Einstein made the following assumptions:

Assumptions. (*i*) The atoms are identical independent simple harmonic oscillators.

(*ii*) All atoms vibrate in identical environments and have the same natural frequency.

(*iii*) The energy spectrum of atomic oscillators is not continuous as assumed in classical theory but has discrete values as given by quantum theory. According to this theory an oscillator of frequency ν has only *discrete* values of energy given by $E_n = nh\nu$ where $n = 0, 1, 2 \ldots$ etc., called quantum number, h the Planck's constant = 6.63×10^{-34} Joule-sec.

(*iv*) The vibration of each atom in the solid may be resolved into components along three perpendicular axes so that each atom is represented by *three* harmonic oscillators. Thus a solid containing N atoms is considered to be equivalent to $3N$ harmonic oscillators.

(*v*) The oscillators form an assembly of systems which are distinguishable (or identifiable) due to their location at separate and distinct lattice sites in the crystal. These, therefore, obey Maxwell Boltzmann statistics and have corresponding distribution of energy.

Lattice heat capacity. According to above assumptions the *relative probability* that the (atomic) oscillator has the energy $E_n = nh\nu$ at the temperature T is given by Boltzmann's distribution of energy function $e^{-E_n/kT}$.

To find $\bar{E}$ the *average* energy of the oscillator find the sum of $E_n e^{-E_n/kT}$ over all n from $n = 0$ to $n = \infty$, *i.e.*,

$$\sum_{n=0}^{n=\infty} E_n e^{-E_n/kT}$$

and divide the result by the sum of $e^{-E_n/kT}$ over all n from $n = 0$ to $n = \infty$, *i.e.*,

$$\sum_{n=0}^{n=\infty} e^{-E_n/kT}$$

$$\therefore \quad \bar{E} = \frac{\sum_{n=0}^{n=\infty} E_n e^{-E_n/kT}}{\sum_{n=0}^{n=\infty} e^{-E_n/kT}} = \frac{\sum_{n=0}^{n=\infty} nh\nu\, e^{-nh\nu/kT}}{\sum_{n=0}^{n=\infty} e^{-nh\nu/kT}}$$

$$= \frac{h\nu\,[0 + e^{-h\nu/kT} + 2e^{-2h\nu/kT} + \ldots\ldots \text{to } \infty]}{[1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots\ldots \text{to } \infty]}$$

Substituting $-h\nu/kT = x$, we have

$$\bar{E} = \frac{h\nu\,[0 + e^{x} + 2e^{2x} + \ldots\ldots \text{to } \infty]}{[1 + e^{x} + e^{2x} + \ldots\ldots \text{to } \infty]}$$

Each term in the numerator is the differential coefficient of the corresponding term in the denominator.

$$\therefore \quad \bar{E} = h\nu \frac{d}{dx} \ln [1 + e^{x} + e^{2x} + \ldots\ldots \text{to } \infty]$$

Now, $1 + e^{x} + e^{2x} + \ldots\ldots$ to ∞ is a geometric series having first term 1 and common ratio e^{x}.

The sum of the series to $\infty = \frac{1}{1 - e^{x}}$.

and $$\ln \frac{1}{1 - e^{x}} = -\ln (1 - e^{x})$$

$$\bar{E} = -h\nu \frac{d}{dx} \ln (1 - e^{x})$$

$$= \frac{h\nu e^{x}}{1 - e^{x}} = h\nu \frac{1}{e^{-x} - 1} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

According to wave mechanics the ground state energy of a harmonic oscillator is not zero but $\frac{1}{2} h\nu$ and thus the energy of subsequent states is given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu$$

If we start with this value of E_n, we get

$$\bar{E} = h\nu \left(\frac{1}{2} + \frac{1}{e^{h\nu/kT} - 1}\right)$$

The term $\frac{1}{2} h\nu$ is temperature independent and gives the value of $\bar{E}$ at $T = 0$. In other words according to quantum mechanics, the atoms have vibrational energy even at absolute zero. However this term does not make any contribution to the specific heat (or lattice heat capacity).

If N_0 is the number of atoms in a kilo-mole, it is equivalent to $3N_0$ oscillators (See assumption *iv*) and the total energy

$$U = 3N_0 \bar{E} = \frac{3N_0 h\nu}{e^{h\nu/kT} - 1}$$

and molar lattice heat capacity

$$C_v = \left(\frac{dU}{dT}\right)_v = 3N_0 k \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad \ldots(i)$$

This result can be put in a simple form by substituting $h\nu/k = \theta_E$ known as Einstein temperature in the above relation and, get

$$C_v = 3N_0 k \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad \ldots(ii)$$

The frequency ν of the atomic oscillator corresponding to Einstein temperature θ_E is known as Einstein frequency or frequency of Einstein oscillator and is given by

$$\nu = \frac{k\theta_E}{h}$$

Predictions and comparison with experimental results

(*i*) At *high temperatures* the relation

$$\bar{E} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

reduces to the relation $\bar{E} = kT$ because for large values of T, $h\nu \ll kT$ and

$$e^{h\nu/kT} = 1 + \frac{h\nu}{kT} + \ldots\ldots \qquad \left[\because e^{x} = 1 + x + \frac{x^2}{2!} + \ldots\right]$$

neglecting higher powers.

$$\bar{E} = \frac{h\nu}{1 + \frac{h\nu}{kT} - 1} = kT$$

and

$$C_v = \frac{dU}{dT} = \frac{d}{dT}(3N_0\bar{E}) = 3N_0 k = 3R$$

i.e., the lattice heat capacity at high temperatures approaches the classical value $3R$. This is in fair agreement with experimental results.

(*ii*) *At low temperatures.* As T decreases $\bar{E}$ falls off rapidly and at very low temperatures $h\nu >> kT$ so that

$$e^{h\nu/kT} >> 1 \text{ and } e^{h\nu/kT} - 1 = e^{h\nu/kT}$$

Making this approximation relation (*i*) becomes

$$C_v = 3N_0 k \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT})^2}$$

$$= 3N_0 k \left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT} = 3R \left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT}$$

$$= 3R \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$$

i.e., the lattice heat capacity is proportional to $e^{-h\nu/kT}$ $(e^{-\theta_E/T})$ which is the dominant factor and in the limit approaches zero as $T \to 0$.

This is not in agreement with experimental observations because it has been observed that for most of the solids the heat capacity at very low temperatures varies at T^3, *i.e.*, it obeys the T^3 law.

(*iii*) If we plot a graph between C_v and T/θ_E, we find that Einstein curve fits the experimental results fairly well at all temperatures except very low temperatures in the range of liquid helium. The Einstein temperature θ_E distinguishes between the high temperature and low temperature behaviour.

(*iv*) Einstein assumed the atoms in the crystal to be independent oscillators but this is not in conformity with actual facts. As each atom is under the influence of the field of force of a number of other vibrating atoms the situation is a very complex one.

Q. 4.9. (*a*) What is Einstein temperature? ***(P.U. 2001)***

(*b*) Calculate Einstein temperature given Einstein frequency as 9×10^{11} Hz. ***(H.P.U. 2001)***

(*c*) Calculate the frequency of Einstein oscillator for $\theta_E = 236$ K. Given $k_B = 1.38 \times 10^{-23}$ JK^{-1} and $h = 6.6 \times 10^{-34}$ J sec. ***(M.D.U. 2000)***

(*d*) Discuss as why Einstein's theory of lattice heat capcity is not capable of giving correct behaviour at low temperatures.*(H.P.U. 2002)*

Ans. (*a*) **Einstein temperature.** According to Einstein theory of lattice heat capacity, the atoms of a solid are identical independent simple harmonic oscillators having a frequency ν and energy $E = n h\nu$ where n is an integral number 0, 1, 2, ... etc. known as quantum number. According to this theory, the molar lattice heat capacity at a temperature T is given by

$$C_v = 3N_0 k \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{[e^{h\nu/kT} - 1]^2}$$

The quantity $\frac{h\nu}{k} = \theta_E$ is known as **Einstein temperature** and the corresponding value of ν is known as **Einstein frequency** or frequency of Einstein oscillator.

(*b*) Einstein frequency $\nu = 9 \times 10^{11}$ Hz

$$\therefore \text{Einstein temperature } \theta_E = \frac{h\nu}{k} = \frac{6.6\times10^{-34}\times9\times10^{11}}{1.38\times10^{-23}}$$

$$= 43\text{K}$$

(*c*) Einstein temperature $\theta_E = 236\text{K}$

Now, $\theta_E = \frac{h\nu}{k}$

$$\therefore \text{Frequency of Einstein oscillator } \nu = \frac{k\theta_E}{h} = \frac{1.38\times10^{-23}\times236}{6.6\times10^{-34}}$$

$$= 49.34 \times 10^{11}\text{ Hz}$$

(*d*) For answer See **Q. 4.11 Basic draw backs of Einstein Model.**

Q. 4.10. Why does Dulong and Petit's law fail at low temperature?

(G.N.D.U. 2004; Pbi. U. 2001; H.P.U. 1997)

Ans. According to Einstein's theory of specific heat the total energy is given by

$$U = 3N_0\bar{E} = 3N_0\frac{h\nu}{e^{h\nu/kT}-1} \quad \ldots (i)$$

and

$$C_v = \frac{dU}{dT} = 3N_0k\left(\frac{h\nu}{kT}\right)^2\frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} \quad \ldots (ii)$$

The photon energy $h\nu$ indicates the difference between the allowed energies of the oscillator. At very high temperatures $h\nu/kT$ is a very small quantity and hence

$$e^{h\nu/kT} = 1 + \frac{h\nu}{kT} + \ldots\ldots \text{ higher powers}$$

$$\therefore \quad e^{h\nu/kT} - 1 = 1 + \frac{h\nu}{kT} - 1 = \frac{h\nu}{kT}$$

Substituting in (*i*), we get

$$U = 3N_0h\nu\frac{kT}{h\nu} = 3N_0kT$$

$$\therefore \quad C_v = \frac{dU}{dT} = 3N_0k = 3R$$

i.e., Dulong and Petit's law is obeyed.

At low temperatures $\frac{h\nu}{kT}$ is a large quantity and unity can be neglected as compared to $e^{h\nu/kT}$

$$\therefore \quad e^{h\nu/kT} - 1 = e^{h\nu/kT}$$

Substituting in equation (*ii*), we have

$$C_v = 3N_0k\left(\frac{h\nu}{kT}\right)^2\frac{e^{h\nu/kT}}{(e^{h\nu/kT})^2} = 3N_0k\left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT}$$

Hence C_v is proportional to $e^{-h\nu/kT}$, *i.e.*, Dulong and Petit's law fails at low temperatures.

Q. 4.11. What are the basic drawbacks of Einstein model of specific heat? Explaining the assumptions clearly, derive an expression for the lattice specific heat according to Debye model. Discuss the high and low temperature limits and define Debye's T^3 law. Give limitations (drawbacks) of Debye model. Compare Debye model with Einstein model.

(P.U. 2004, 2003, 2001, 1999, 1995, 1994; Pbi.U. 2004, 2000, 1999, 1997; G.N.D.U. 2004, 1999, 1997; H.P.U. 2003, 2002, 2001, 2000, 1997, 1996, 1995; M.D.U. 2003, 2001; Calicut U. 2003; Kolkata U. 2002, 1992; K.U. 2000)

Ans. Basic drawbacks of Einstein model. In Einstein model of lattice specific heat of solids each atom is supposed to vibrate as a single unit independently of its neighbours. The vibrational motion of the crystal as a whole was considered to be the same as the vibrational motion of a single atom and, therefore, all the atomic vibrations of the crystal were assigned a common frequency ν which is the natural frequency of vibration of a single atom. This assumption is, however, over simplified because the atoms in a crystal are bound together to form a system of *coupled oscillators* which cannot vibrate independently. Each atom is under the influence of the field of force of a number of other vibrating atoms. This is why Einstein's theory of lattice heat capacity was not capable of giving correct behaviour particularly at low temperatures.

Assumptions of Debye model of lattice specific heat

1. In Einstein's theory of specific heat of solids each atom is supposed to vibrate as a single unit independently of its neighbours. But the situation is not so simple as each atom is under the influence of the field of force of a number of other vibrating atoms.

Debye took into account the effect of *coupling* between adjacent atoms and considered the *solid as a continuous elastic body*.

2. According to Debye the internal energy of a solid instead of residing in the vibrations of individual atoms was present in the *elastic standing waves* produced due to the vibrations of individual atoms.

3. Debye assumed that the *energy* of these elastic standing waves was *quantised*. A quantum of vibrational energy is called a *phonon*. It has an energy $h\nu$ simular to that of a *photon* where ν is the frequency of vibration and h Planck's constant. A *phonon* travels with the speed of sound as sound waves are elastic waves in nature.

4. The number of possible vibrational modes of any kind in the frequency range ν and $(\nu + d\nu)$ is given by $Z(\nu)\,d\nu = \left(\frac{4\pi V}{v^3}\right)\nu^2\,d\nu$ where $Z(\nu)$ is the number of vibrational modes per unit frequency range and is known as *density of modes*, $V = L^3$ is the volume of the solid taken in the form of a cube of each side L and v the velocity of propagation of the wave through the medium.

5. We shall first calculate the *density of vibrational modes* of crystal treating it as a continuous medium.

Density of modes. For simplicity we shall consider one dimensional continuous string of length L. Suppose the string is fixed at both the ends and is vibrating. If the displacement of the string at any point x at any instant of time t is $u(x, t)$, then the wave equation is given by

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \quad \ldots (i)$$

where v is the velocity of propagation of the wave in the string.

Since both the ends of the string are fixed, the solution of Eq. (*i*) corresponds to standing waves.

$$u(x, t) = A \sin\left(\frac{n\pi}{L} x\right) \cos 2\pi \nu_n t \quad \ldots (iii)$$

where n is a positive integer ≥ 1. The length of the string L is an integral multiple of half wavelengths

$$\therefore \quad L = n \frac{\lambda_n}{2}$$

or $$\lambda_n = \frac{2L}{n}$$

$$\therefore \text{ Frequency } \nu_n = \frac{v}{\lambda_n} = \frac{nv}{2L} \quad \ldots (iii)$$

This shows that the frequency of the string can have discrete values only which are integral multiples of $\frac{v}{2L}$.

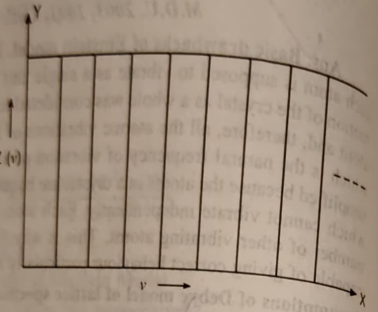

Fig. 4.10

For example, $\nu_1 = \frac{v}{2L}$, $\nu_2 = \frac{v}{L}$;

$$\nu_3 = \frac{3v}{2L} \text{ etc.,}$$

i.e., the frequency spectrum of the continuous string is discrete and contains an infinite number of parallel lines equidistant from each other as shown in Fig. 4.10.

From Eq. (*iii*) $$n = \frac{2L}{v} \nu_n$$

$$\therefore \quad dn = \frac{2L}{v} d\nu_n \quad \ldots (iv)$$

Eq. (*iv*) gives the number of possible modes of vibration in a frequency interval $d\nu$.

Three dimensional case. If we consider a three dimensional case the wave equation (*i*) takes the three dimensional form

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \quad \ldots (v)$$

Taking the three dimensional continuous medium as a cube of side L, with fixed faces, the standing wave solution of the standing wave equation (*v*) becomes

$$u(x, y, z, t) = A \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \cos 2\pi \nu t \quad \ldots (vi)$$

where n_x, n_y and n_z are positive integers ≥ 1.

Differentiating Eq. (*vi*) twice with respect to x, we get

$$\frac{\partial^2 u}{\partial x^2} = -\left(\frac{n_x \pi}{L}\right)^2 A \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \cos 2\pi \nu t$$

$$= -\left(\frac{n_x \pi}{L}\right)^2 u(x, y, z, t)$$

Similarly differentiating Eq. (*vi*) twice with respect to y and z respectively, we get

$$\frac{\partial^2 u}{\partial y^2} = -\left(\frac{n_y \pi}{L}\right)^2 u(x, y, z, t)$$

$$\frac{\partial^2 u}{\partial z^2} = -\left(\frac{n_z \pi}{L}\right)^2 u(x, y, z, t)$$

and $$\frac{\partial^2 u}{\partial t^2} = -(2\pi\nu)^2 u(x, y, z, t)$$

Substituting these values in Eq. (*v*), we get

$$\left(\frac{n_x \pi}{L}\right)^2 + \left(\frac{n_y \pi}{L}\right)^2 + \left(\frac{n_z \pi}{L}\right)^2 = \frac{1}{v^2} 4\pi^2 \nu^2 = \frac{4\pi^2}{\lambda^2}$$

or $$\frac{\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{4\pi^2 \nu^2}{v^2} = \frac{4\pi^2}{\lambda^2}$$

or $$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2 \nu^2}{v^2} \quad \ldots (vii)$$

This equation gives the possible modes of vibration. The integers n_x, n_y and n_z determine the possible frequencies (or wavelengths).

In order to determine the possible modes of vibration $Z(\nu)\, d\nu$ in the frequency interval between ν and $(\nu + d\nu)$, we consider a network of points, the position of each point being given by three Cartesian positive integer coordinates n_x, n_y and n_z. Thus the radius vector R from the origin to any point is given by

$$R^2 = n_x^2 + n_y^2 + n_z^2 \quad \ldots (viii)$$

[This is the equation of a sphere in integral space]

From Eq. (*vii*) and (*viii*), we get

$$R^2 = \frac{4L^2 \nu^2}{v^2} \quad \ldots (ix)$$

$$\therefore \quad R = \frac{2L}{v} \nu$$

and $$dR = \frac{2L}{v} d\nu \quad \ldots (x)$$

As each point occupies, on the average, a unit volume in the integer space, the number of points in the spherical shell between radii R and $(R + dR)$ is equal to the volume of an octant of a spherical shell in integer space, *i.e.*, $\frac{1}{8}$ × volume of spherical shell.

$$\therefore \text{ Volume of octant of spherical shell} = \frac{1}{8} \times 4\pi R^2\, dR$$

Therefore, the number of possible modes of vibration, *i.e.*, frequencies being between ν and $(\nu + d\nu)$ are given by

$$Z(\nu)\, d\nu = \frac{4\pi}{8} R^2\, dR \quad \ldots (xi)$$

Substituting the value of R^2 from Eq. (*ix*) and dR from Eq. (*x*) in Eq. (*xi*), we get,

$$Z(\nu)\,d\nu = \frac{4\pi}{8} \times \frac{4L^2\nu^2}{v^2} \cdot \frac{2L}{v}\,d\nu$$

$$= 4\pi \frac{L^3}{v^3}\,\nu^2\,d\nu$$

But $L^3 = V$ the volume of the cube. Therefore, the number of modes of vibration between ν and $(\nu + d\nu)$ are

$$Z(\nu)\,d\nu = \left(\frac{4\pi V}{v^3}\right)\nu^2\,d\nu \qquad \ldots (xii)$$

In general there are two kinds of elastic waves that can occur in a solid, *viz.*, *longitudinal waves* having a velocity v_l and *transverse* waves having a velocity v_t. The velocity of propagation v_t of transverse waves is generally different from the velocity of propagation v_l of longitudinal waves. Again transverse waves have two perpendicular directions of polarisation or two vibrational modes perpendicular to the direction of propagation, whereas the longitudinal waves have only one mode which lies along the direction of propagation.

In such a case the total number of vibrational modes is given by

$$Z(\nu)\,d\nu = 4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]\nu^2\,d\nu \qquad \ldots (xiii)$$

6. **Debye approximation.** If the interatomic distance is small as compared to the wave length of elastic waves, the crystal can be regarded as a continuum from the point of view of the wave. Debye, therefore, assumed that the continuum model was applicable to all possible vibrational modes of the crystal. As the crystal consists of a finite number of atoms (N) the total number of vibrational modes is taken to be $3N$. This fact, puts an upper limit to the frequency of the elastic waves which can propagate through the crystal. This highest frequency propagating through a crystal is known as *Debye frequency*. It is common to longitudinal and transverse modes of vibration. Thus the frequency spectrum corresponding to the perfect continuum is cut off at Debye frequency ν_D so as to comply with a total of $3N$ modes as shown in Fig. 4.11. Thus Debye frequency can be determined by equating the total number of possible vibrations to $3N$.

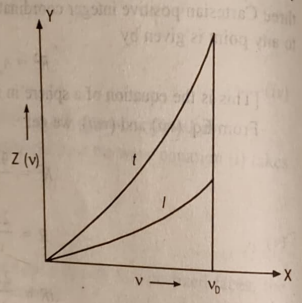

Fig. 4.11

Hence $$\int_0^{\nu_D} Z(\nu)\,d\nu = 3N$$

But according to Eq. (*xiii*),

$$Z(\nu)\,d\nu = 4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]\nu^2\,d\nu$$

$$\therefore \int_0^{\nu_D} 4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]\nu^2\,d\nu = 3N$$

or $$4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]\frac{\nu_D^3}{3} = 3N$$

or $$\nu_D^3 = \frac{9N}{4\pi V}\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]^{-1} \qquad \ldots (xiv)$$

7. Debye further assumed that phonon gas behaves like a photon gas and average energy E per standing wave at a temperature T is given by

$$E = \frac{h\nu}{e^{h\nu/kT} - 1}$$

If a quantum harmonic oscillator is associated with each vibrational mode of the same frequency, the vibrational energy of the crystal is given by

$$U = \int_0^{\nu_D} EZ(\nu)\,d\nu = \int_0^{\nu_D} Z(\nu)\frac{h\nu}{e^{h\nu/kT} - 1}\,d\nu$$

Substituting the value of $Z(\nu)\,d\nu$ from Eq. (*xiii*), we get

$$U = \int_0^{\nu_D} 4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]\frac{h\nu^3}{e^{h\nu/kT} - 1}\,d\nu$$

$$= 4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]\int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/kT} - 1}\,d\nu \qquad \ldots (xv)$$

From Eq. (*xiv*),

$$4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v_d^3}\right] = \frac{9N}{v_D^3}$$

Substituting in Eq. (*xv*), we get

$$U = \frac{9N}{v_D^3}\int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/kT} - 1}\,d\nu \qquad \ldots (xvi)$$

Substituting $\frac{h\nu}{kT} = x$ and $\frac{h\nu_D}{kT} = x_m$, we get

$$\nu = \frac{x\,kT}{h} \quad \therefore \quad d\nu = \frac{kT}{h}\,dx$$

Eq. (*xvi*), therefore, becomes,

$$U = \frac{9Nh}{v_D^3}\left(\frac{kT}{h}\right)^4 \int_0^{x_m} \frac{x^3}{e^x - 1}\,dx$$

$$= 9N\left(\frac{kT}{h\nu_D}\right)^3 kT \int_0^{x_m} \frac{x^3}{e^x - 1}\,dx$$

We now introduce a characteristic temperature θ_D, known as *characteristic Debye temperature* given by $\theta_D = \frac{h\nu_D}{k}$

$$x_m = \frac{\theta_D}{T}$$

$$\therefore \quad U = 9NkT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1}\,dx \qquad \ldots (xvii)$$

and

$$= 9RT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1}\,dx \qquad \ldots (xvii)(a)$$

when N is Avogadro's number.

Specific heat. From Eq. (*xvii*), we get

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 9NK\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2}\,dx$$

$$= 3R\left(\frac{\theta_D}{T}\right) F_D$$

where

$$F_D = 3\left(\frac{T}{\theta_D}\right)^4 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2}\,dx \qquad \ldots (xviii)$$

The function is called *Debye function*.

Predictions (or successes). On the basis of above assumptions Debye predicted the variation of specific heat with temperature, particularly at very high and very low temperatures.

1. **For very high temperatures.** At very high temperatures ($T >> \theta_D$), $x = \frac{h\nu}{kT}$ has a very small value so that $e^x = 1 + x$ and $\frac{x^3}{e^x - 1} = x^2$ and $\int_0^{\theta_D/T} x^2\,dx = \left[\frac{x^3}{3}\right]_0^{\theta_D/T} = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$

Substituting these values in Eq. (*xvii*), we get

$$U = 9NkT\left(\frac{T}{\theta_D}\right)^3 \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

$$= 3NkT$$

$\therefore$ Specific heat at constant volume $\qquad \ldots (xix)$

$$C_v = \frac{dU}{dT} = 3Nk = 3R$$

This is Dulong and Petit's law. Thus at very high temperatures Debye's theory agrees with both the classical and Einstein's quantum theory results. In other words, quantum considerations are of no importance at high temperatures.

2. **At very low temperatures.** At very low temperatures ($T << \theta_D$)

$$x_m = \frac{\theta_D}{T} \to \infty \text{ and } \int_0^{\theta_D/T} \to \int_0^{\infty}$$

$$\therefore \quad \int_0^{\theta_D/T} \frac{x^3}{e^x - 1}\,dx = \int_0^{\infty} \frac{x^3}{e^x - 1}\,dx = \frac{\pi^4}{15}$$

which on substituting in Eq. (*xvii*) (*a*) gives

$$U = 9RT\left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3}{5}\pi^4 R\frac{T^4}{\theta_D^3}$$

$\therefore$ Specific heat at constant volume

$$C_v = \frac{dU}{dT} = \frac{12}{5}\pi^4 \frac{R}{\theta_D^3} T^3 = 234R\left(\frac{T}{\theta_D}\right)^3 \qquad \ldots (xx)$$

Debye's T^3 law. From relation (*xx*) we find that the specific heat is proportional to T^3 at very low temperatures as $\theta_D = \frac{h\nu_m}{k}$ = a constant for the substance. This is *Debye's T^3 law*. This law has been verified for a number of substances and experimentally observed values agree remarkably with theoretical values. This law holds for $T \le \frac{\theta_D}{10}$.

Limitations (drawbacks or failures) of Debye model. 1. The Debye's continuum model is valid for long wavelengths only, *i.e.*, only low frequencies are active in the solid. Thus this theory neglects the dispersion of waves.

2. The total number of vibrational modes are assumed to be $3N$. As the solid is taken to be an elastic continuum, it should have an infinite number of frequencies.

3. The cut off frequency ν_D is assumed to be the same for both longitudinal and transverse waves. But as the velocities v_l and v_t are unequal, there should be two different values of ν_D for transverse and longitudinal waves.

4. The experimental results agree with the results from Debye's theory of specific heat fairly well at high temperatures.

At low temperatures Debye's T^3 law does not hold in the temperature range $\le 0.1\,\theta_D$.

According to Debye's theory $\theta_D = \frac{h\nu_D}{k}$ is independent of temperature but actually θ_D is found to vary up to 10% with temperature.

5. This theory assumes that the solid consists of identical atoms. Hence the theory is not applicable to crystals where the atoms are not identical, *e.g.*, *NaCl*.

6. Debye's theory completely neglects the inter-atomic interaction and electronic contribution to lattice specific heat.

Comparison with Einstein model. 1. At high temperatures both Debye and Einstein models give the same result $C_v = 3R$ which agrees with classical result of Dulong and Petit.

2. At low temperatures Einstein's theory predicts $C_v \propto e^{-h\nu/kT}$ whereas Debye's theory predicts $C_v \propto T^3$ which is more closely in agreement with experimental results. Thus, Einstein's theory fails at low temperatures. For example, for silver at 14 *K* the value calculated from Einstein's formula is almost 28 times lower than the experimental value. Einstein assumed that atoms vibrate independently in the presence of other atoms with a constant frequency corresponding to optical branch whereas Debye proposed that waves could be propagated through solids and their frequencies ranged from a lower value corresponding to sound waves to a higher value corresponding to infra-red part of electromagnetic spectrum. He considered the vibrational mode of a crystal as a whole.

Q. 4.12. (*a*) Describe Debye's T^3 law of specific heat of solids. ***(G.N.D.U. 2002, 2000; Pbi.U. 2000; P.U. 2000)***

5 Free Electron Theory of Metals

Q. 5.1. (*a*) What is meant by free electron gas model of metals? Define free electron Fermi gas. Which properties of solids are explained by free electron gas theory?
(G.N.D.U. 2004, 1992; Pbi. U. 2004, 2002, 2001, 1999, 1997; P.U. 2003, 2001, 1997; H.P.U. 2000, 1996)

(*b*) How far the free electron theory is inferior or superior to band theory? Discuss the successes and failures of these theories. ***(Pbi. U. 2002, 2000, 1999; G.N.D.U. 1992)***

Ans. (*a*) Free electron gas model. A number of important physical properties of metals can be explained in terms of '*free electron model*'. According to this model the *most weakly bound valence electrons* of the metal become the *conduction electrons*. The forces between the conduction electrons and ion cores are neglected. The total energy is all kinetic, the potential energy is also neglected. Hence the conduction electrons move about within the metal freely without any collisions similar to the molecules of an ideal gas.

It should be, however, noted that the `*electron gas*' is charged while ordinary gas is generally neutral. Secondly, the electron concentration in metals is much higher than that in ordinary gas.

The simplest metals are alkali metals. For example, in *Na* atom ($1s^2\ 2s^2\ 2p^6\ 3s^1$) the valence electron is in a $3s$ state. In the metal this electron becomes a conduction electron moving throughout the metal crystal. The remaining 10 electrons of Na^+ ion core fill the $1s$, $2s$ and $2p$ states having 2, 2 and 6 electrons respectively in the free ion, the distribution of core electrons being *essentially* the *same* in the free ion as in the metal.

The *metal crystal* is thus supposed to consist of positive metal ions with free electron gas of valence electrons of the atom *permeating* the space between the positive ions. These free electrons behave like the atoms or molecules in a perfect gas and are, therefore, sometimes known as '*free electron gas*' or '*fermi gas*' or '*Electron cloud*'.

Free electron Fermi gas. By a *free electron Fermi gas* we mean a gas of free and non-interacting electrons subject to Pauli's exclusion principle.

Interpretation of metallic properties. The interpretation of metallic properties in terms of free electron gas model was developed by Drude and Lorentz on the basis of classical theory applying Maxwell Boltzmann statistics to the electron gas. The mutual repulsion between the negatively charged electrons was neglected and the potential field due to the positive ion core was assumed to be constant everywhere. Thus this theory could explain:

(*i*) *Ohm's law i.e.*, the current i is proportional to potential difference E

$$i \propto E \text{ or } \frac{E}{i} = R \text{ (a constant)}$$

(*ii*) For *pure metals* electrical conductivity σ is inversely proportional to absolute temperature

$$\sigma \propto \frac{1}{T}$$

but for *impure metals* electrical conductivity is inversely proportional to the square root of absolute temperature

$$\sigma \propto \frac{1}{\sqrt{T}}$$

(*iii*) For most of the metals the resistivity ρ is inversely proportional to pressure p

$$\rho \propto \frac{1}{p}$$

(*iv*) The ratio of thermal conductivity K to electrical conductivity σ is proportional to absolute temperature

$$\sqrt{\frac{K}{\sigma}} \propto T$$

This is known as *Wiedemann-Franz* law.

(*v*) A very characteristic property of metals is their *complete opacity* and *high lustre*.

A metal behaves like an opaque body because when light energy falls on a metal crystal, the free electrons are set into forced oscillation having the same frequency as the incident light. In this way the whole of the light is absorbed and hence the metal behaves as an opaque body.

Metals have high lustre because the incident light makes the free electrons go to the excited states. When these electrons come back to the initial state they emit light of the same energy as was absorbed initially. Thus the metal appears to reflect virtually all the light incident on it which given it the characteristic metallic lustre.

(*vi*) The specific heat and paramagnetism of metals can be understood on the basis of interaction between free electrons and external energy source, whether thermal or magnetic in nature. The results predicted on the basis of classical theory, using Maxwell Boltzmann statistics were much larger than the actually observed values. However, making use of quantum mechanics and Fermi-Dirac statistics, it was found that resulting values of specific heat and paramagnetic susceptibility were in much better agreement with experimental results.

(*b*) **Comparison with band theory.** The free electron theory is very useful in explaining experimental facts that essentially depend upon the kinetic properties of conduction electrons and in this respect is *superior* to band theory.

For example, the free electron theory conveniently explains the properties of metals like specific heat, thermal conductivity, electrical conductivity, Ohm's law, magnetic susceptibility, Wiedemann-Franz law, complete opacity of metals and their high lustre etc.

The free electron theory is unable to explain the properties which depend upon the interaction of electrons with neighbouring atoms or ions and in this respect is *inferior* to band theory.

For example, the model fails to explain the distinction between metals, semi-metals, semi-conductors and insulators and why some crystals are metallic. It does not explain the occurrence of positive values of Hall effect, the relation between conduction electrons in the metal to the valence electrons in the free atom.

The theory also fails to correctly predict the temperature dependence of resistivity. According to this theory, resistivity varies as $\sqrt{T}$ whereas actually it is found to vary linearly with temperature.

The theory could not correctly explain the heat capacity and paramagnetic susceptibility of conduction electrons.

It does not explain the occurrence of long mean free paths of the order of $10^8 - 10^9$ inter-atomic space or more than one cm at low temperatures.

All these properties can be explained on the basis of band theory according to which electrons in crystals are arranged in energy bands separated by energy gaps or band gaps. This band gap arises from the interaction of conduction electron waves with ion cores of the crystal.

Q. 5.2. (*a*) What are static and transport properties in the case of free electron model? ***(Pbi. U. 2004; H.P.U. 2002)***

(*b*) Obtain an expression for the electrical conductivity of a metal on the basis of free electron theory. Hence prove Ohm's law.

(Bang. U. 2004, 2000; Luck. U. 2002, Gharwal U. 2000)

Ans. (*a*) The electronic properties of metals are broadly studied under two heads.

(*i*) Static properties, (*ii*) Transport properties.

(*i*) **Static properties.** The static properties are those properties which can be treated effectively by considering the energy levels only or the distribution of energy levels to which the electrons belong. These properties include, various electron emission properties, magnetic properties and properties like heat capacity and contact potential. These properties arise as a result of the excitation of electrons by light, thermal energy, strong electric and magnetic fields.

(*ii*) **Transport properties.** The transport properties are those which can be treated by considering the detailed response of the electrons to an external field *i.e.*, by taking into consideration the properties due to the acceleration of electrons such as electrical and thermal conductivity, Hall effect, thermoelectric effect etc.

(*b*) **Electrical conductivity.** *Electrical conductivity is defined as the quantity of electricity (charge q) that flows in a unit time through a unit area of cross-section of the conductor per unit potential gradient (or electric field).*

If a charge q flows through a conductor of area of cross-section A in a time t under an electric field E, then

$$\text{Electrical conductivity } \sigma = \frac{q}{AtE}$$

According to free electron model, the electrons in a solid move freely. If e is the charge, m the mass of the electron and E the applied electric field, then acceleration produced in the electron

$$a = \frac{d^2x}{dt^2} = \frac{Ee}{m}$$

Integrating, we have

$$v = \frac{dx}{dt} = \frac{Eet}{m} + C$$

At $t = 0$, $\frac{dx}{dt} = 0$ $\quad \therefore C = 0$

$$\therefore \quad v = \frac{Eet}{m} \qquad \ldots(i)$$

and Energy of the electron $= \frac{1}{2}mv^2$.

If T is the absolute temperature and k Boltzmann's constant, then

$$\text{Energy of the electron} = \frac{3}{2}kT$$

$$\therefore \quad \frac{1}{2}mv^2 = \frac{3}{2}kT$$

or $$mv = \frac{3kT}{v} \qquad \ldots(ii)$$

Ans. Mass of 1 atom of Cu = 63.5 a.m.u. = $63.5 \times 1.66 \times 10^{-27}$ Kgm.

Mass of 1 m^3 of Cu = Density of copper = 8.94×10^3 Kg/m^3

$$\therefore \quad \text{Number of atoms per m}^3 = \frac{8.94 \times 10^3}{63.5 \times 1.66 \times 10^{-27}} = 8.48 \times 10^{28}$$

As each Cu atom contributes one electron, the number of electrons per unit volume

$$\frac{N}{V} = 8.48 \times 10^{28}$$

Fermi energy

$$E_f = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3} = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

$$= \frac{6.63 \times 10^{-34} \times 6.63 \times 10^{-34}}{8 \times 9.1 \times 10^{-31}}\left[\frac{3 \times 8.48 \times 10^{28}}{\pi}\right]^{2/3}$$

$$= \frac{6.63 \times 6.63 \times 10^{-68} \times 18.7 \times 10^{18}}{8 \times 9.1 \times 10^{-31}}$$

$$= 11.3 \times 10^{-19} \text{ J} = 7.06 \text{ eV}.$$

Q. 5.19. What is the cause of failure of free electron theory? ***(P.U. 2000)***

Ans. Failure of free electron theory. The free electron theory was successful in explaining various electronic and thermal properties of metals like heat capacity, thermal and electrical conductivity, magnetic susceptibility etc. However, there are some other properties which could not be explained by this theory. For example:–

(*i*) The theory could not explain why certain solids have a large number of free electrons and behave as good conductors, while certain others have hardly any free electrons and behave as insulators.

(*ii*) The theory could not explain the properties of semi-conductors.

(*iii*) It is found that divalent metals like *Be*, *Cd* etc. and trivalent metals like *Al*, *In* etc. are not good conductors. On the other hand, some monovalent metals are good conductors although these metals have a much smaller concentration of electrons as compared to divalent and trivalent metals.

(*iv*) According to this theory, the shape of the Fermi surface should be spherical but it is found to be non-spherical.

(*v*) Some of the metals like *Be* and *Zn* exhibit positive Hall co-efficient while the free electron theory predicts negative Hall effect for all metals.

The failure of the free electron theory is due to the over simplified assumption that the conduction electrons in a metal move in a region of zero or constant potential due to ion cores and are free to move about in the metal crystal – the motion being retarded only by the surface of the crystal. In fact, the potential due to ion cores is not constant and changes with the position of the electron in the crystal in a complicated manner. Some contributions to potential also arises due to the presence of other electrons in the metal crystal which has not been considered.

To a reasonable approximation the ion cores may be considered at rest and the potential experienced by the electron in a metal crystal assumed to be periodic with a period equal to lattice constant. This periodic potential is supposed to extend upto infinity in all directions and is interrupted only at the surface of the crystal.

Thus, the failure of the free electron theory of metals was due to the fact that regular arrangement of atoms in a crystal was not taken into account.